

IN THE SPECIFICATION:

Please replace paragraph [0004] with the following.

[0004] Conventional solid composite propellant binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to using cross-linked elastomers as binders. Cross-linked elastomers must be cast within a short period of time after addition of the curative, which time period is known as the ~~“pot life”~~. “pot life.” Disposal of a cast, cross-linked propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems. Furthermore, current state-of-the-art propellant compositions have serious problems that include their use of nonenergetic binders which have lower performance and high end-of-mix viscosities.

Please replace paragraph [0011] with the following.

[0011] ~~It is, therefore, an object of this invention to provide~~ The present invention relates to a thermoplastic elastomer that addresses the aforementioned problems associated with the related art and realizes the advancement expressed above.

Please replace paragraph [0012] with the following.

[0012] In accordance with the principles of this invention, these and other ~~objects~~ advantages are attained by the provision of an energetic thermoplastic elastomer binder that is in a solid state at room temperature and has A blocks and B blocks. The A blocks include one or more polyether(s) derived from monomers of oxetane derivatives and crystalline at temperatures below about 60° C. The B blocks include one or more polyether(s) derived from monomers of oxirane and its derivatives and amorphous at temperatures above about -20° C. The polyoxetane blocks A and polyoxirane blocks B may be linked by end-capping with diisocyanates and linking the end-capped blocks with difunctional linking chemicals in which each of the two terminal functional groups are reactive with an isocyanate moiety of the diisocyanate.

Please replace paragraph [0013] with the following.

[0013] ~~It is also an object of this invention to provide~~ The present invention also relates ~~to a method for the preparation of the above-described energetic thermoplastic binder of this invention.~~ In accordance with the principles of this invention, this and other ~~objects~~ advantages are achieved by a method in which hydroxyl-terminated polyoxetane A ~~blocks~~ blocks, which are crystalline at temperatures below about ~~60° C~~ 60° C, and hydroxyl-terminated polyoxirane B ~~blocks~~ blocks, which are amorphous at temperatures above about ~~-20° C~~ -20° C, are end-capped with a diisocyanate. The diisocyanate preferably has one isocyanate ~~moiety~~ moiety, which is more reactive, preferably at least about five times as reactive, with the terminal hydroxyl group of each of the blocks than the other isocyanate moiety, ~~whereby~~ wherein the more reactive isocyanate moiety tends to react with the terminal-hydroxyl groups of the blocks, leaving the less reactive isocyanate moiety free and unreactive. The end-capped A blocks and the end-capped B blocks are mixed together at approximately the stoichiometric ratios that the blocks are intended to be present in the energetic thermoplastic elastomer. The mixture is reacted with a linking compound having two isocyanate-reactive groups ~~which~~ that are sufficiently unhindered to react with the free and unreacted isocyanate groups of the end-capped blocks. In this manner, the end-capped blocks are linked, but not crosslinked, to form a thermoplastic elastomer.

Please replace paragraph [0014] with the following.

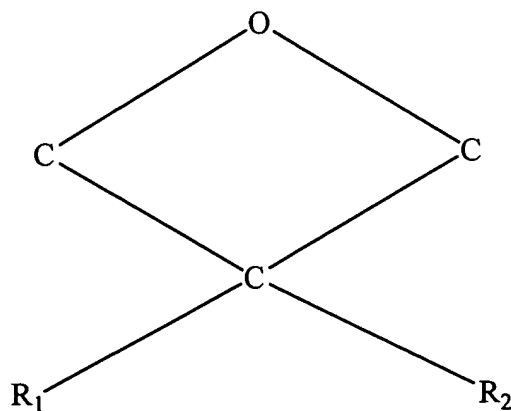
[0014] ~~It is still a further object of this invention to provide~~ The present invention also relates to providing propellants, especially rocket propellants and gun propellants, explosives, gas generants, or the ~~like~~ like, containing the above-discussed energetic thermoplastic elastomer binder or made by procedures including the above-discussed method.

Please replace paragraph [0015] with the following.

[0015] ~~These and other objects, features, and~~ advantages of the present invention will become apparent from the accompanying drawings and following detailed description which illustrate and explain, by way of example, the principles of the present invention.

Please replace paragraph [0017] with the following.

[0017] The thermoplastic elastomer (AB)_n polymers of this invention include A blocks ~~which~~ that are crystalline at temperatures below about 60° C, preferably at temperatures below about 75° C, and B blocks ~~which~~ that are amorphous at temperatures down to about -20° C. Each of the A and B blocks are polyethers derived from cyclic ethers. More specifically, the A blocks are derived from monomers of oxetane derivatives. The B blocks are derived from oxirane monomers and their derivatives, preferably energetic oxirane derivatives. The polymers melt at temperatures between about 60° C and about 120° C, ~~and more preferably 120° C and, more preferably,~~ between about 75° C and about 100° C. The A and B blocks are mutually miscible in the melt. Consequently, the melt viscosity of the block copolymer decreases rapidly as the temperature is raised above the melting point, whereby high energy formulations may include high solids content, e.g., up to about 95% by weight of solid particulates, and can be easily processed. The invention also includes other thermoplastic elastomer block structures, such as ABA tri-block polymers and A_nB star polymers. Contributing to the miscibility of the A and B blocks is their similar chemical structure. Oxetane monomer units used in forming the A blocks of the present invention are generally symmetrically-substituted oxetanes having the general formula:



wherein the R₁ and R₂ groups are preferably the same and are selected from moieties having the general formula: -(CH₂)_nX, where n is 0-10 and X is selected from the group consisting of -H,

-NO₂, -CN, -Cl, -F, -O-alkyl, -OH, -I, -ONO₂, -N(NO₂)-alkyl, -C≡CH, -Br, -CH=CH(H or alkyl), -CO₂-(H or alkyl), -N(H or alkyl)₂, -O-(CH₂)_{1,5}-O-(CH₂)₀₋₈-CH₃, and N₃.

Please replace paragraph [0018] with the following.

[0018] Examples of oxetane derivatives that may be used in forming the A blocks in accordance with this invention are generally symmetrically-substituted oxetanes including, but ~~are not~~ not limited to, the following: BEMO (3,3-bis(ethoxymethyl)oxetane), BCMO (3,3-bis(chloromethyl)oxetane), BMMO (3,3-bis(methoxymethyl)oxetane), BFMO (3,3-bis(fluoromethyl)oxetane), BAOMO (3,3-bis(acetoxymethyl)oxetane), BHMO (3,3-bis(hydroxymethyl)oxetane), BMEMO (3,3-bis(methoxyethoxymethyl)oxetane), BIMO (3,3-bis(iodomethyl)oxetane), BNMO (3,3-bis(nitratomethyl)oxetane), BMNAMO (3,3-bis(methylnitraminomethyl)oxetane), and BAMO (3,3-bis(azidomethyl)oxetane).

Please replace paragraph [0020] with the following.

[0020] Examples of energetic oxiranes that may be used in forming the B blocks in accordance with this invention include, but are not ~~limited to~~ limited to, glycidyl azide polymers (C₃H₅N₃O) (GAP), especially difunctional GAP, and poly(glycidyl nitrate) (C₃H₅NO₄) (PGN). These polymers have a glass transition temperature below about -20° C and are amorphous at temperatures above -20° C.

Please replace paragraph [0025] with the following.

[0001] Thermoplastic elastomers produced in accordance with the present invention may be admixed with other components of a high energy formulation, such as a propellant formulation. The binder system, in addition to the thermoplastic elastomers, may optionally contain one or more plasticizers for improving the resistance of the thermoplastic elastomer to hardening at low temperatures, which may be included at a plasticizer-to-thermoplastic elastomer weight ratio of up to about 1:1. Suitable high energy plasticizers include glycidyl azide polymer (GAP), nitroglycerine, butanetriol trinitrate (BTTN), alkyl nitratomethyl nitramines, trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate, triethylene glycol dinitrate

(TEGDN), bis(dinitropropylacetal/-bis(dinitropropyl)formal (BDNPA/F), and mixtures thereof. Inert plasticizers ~~can~~may also be used. Representative inert plasticizers include, by way of example, dioctyladipate (DOA), isodecylperlargonate (IDP), dioctylphthalate (DOP), dioctylmaleate (DOM), dibutylphthalate (DBP), oleyl nitrile, triacetin, and combinations thereof. The binder system may also contain a minor amount of a wetting agent or lubricant that enables higher solids loading.

Please replace paragraph [0027] with the following.

[0027] The thermoplastic elastomer may be mixed with the solids and other components of high energy formulation at temperatures above its melting temperature. Blending may be ~~done in~~done in a conventional mixing apparatus. Because of the low viscosities of the molten polymer, no solvents are required for blending or other processing, such as extrusion.

Please replace paragraph [0028] with the following.

[0028] An important advantage of having a binder which is meltable is that the elastomer from an outdated device containing the elastomer can be melted down and reused. At the time of such remelting, the binder might be reformulated, e.g., by addition of additional fuel or oxidizer particulates. Accordingly, the thermoplastic elastomer provides for its eventual recycle, as opposed to the burning required for disposal of cross-linked compositions. Because the "pot life" of the thermoplastic propellant exceeds that which would reasonably be required of a propellant or explosive formulation, if any problems develop during casting, the process can be delayed as long as is reasonably necessary, merely by maintaining the formulation in a molten state.

Please replace paragraph [0029] with the following.

[0029] The oxetane homopolymer blocks may be formed according to the cationic polymerization technique taught by Manser in U.S. Patent No. 4,393,199, the complete disclosure of which is incorporated herein by reference. The oxirane homopolymer blocks may be formed according to the technique taught in U.S. Patent No. 5,120,827, the complete

disclosure of which is incorporated herein by reference. The technique employs an adduct of a substance such as a diol, e.g., 1,4-butane diol (BDO), and a catalyst for cationic polymerization, e.g., BF_3 -etherate. This adduct forms with the oxetane monomer being an initiating species ~~which that~~ undergoes chain extension until n moles of monomer have been incorporated in the molecule, n being the ratio of monomers to adduct present. By adjusting the ratio of monomers to adduct present, the average molecular weight of the polymer ~~which that~~ forms may be adjusted. If two or more monomers are present, incorporation of the monomers will be generally random but may depend upon the relative reactivities of the monomers in the polymerization reaction.

Please replace paragraph [0033] with the following.

[0033] Oxetane and oxirane polymer blocks normally have terminal isocyanate-reactive (e.g., hydroxyl) functions which are end-capped with the diisocyanates in accordance with the invention. Preferably, a first of the isocyanate moieties of the end-capping compound is substantially more reactive with the terminal-hydroxyl moieties of the polymer blocks than the other (second) isocyanate moiety. One of the problems with linking these types of polymer blocks is that substituted oxetane-derived hydroxyl end groups units have neopentyl structures, whereby the terminal primary hydroxyl moieties are substantially hindered and therefore less reactive. The blocks derived from oxirane derivatives are secondary alcohols, making their hydroxyl groups less reactive than the primary hydroxyl group of the oxetane-derived A-block. The diisocyanate preferably is selected so that the first of the isocyanate moieties is capable of reacting with a hydroxyl-group of the polymer blocks while the second isocyanate moiety remains free and unreacted. Diisocyanates are preferably used because isocyanates of higher functionality would result in undesirable levels of cross-linking. The different reactivities of the isocyanate moieties ~~is~~ are desirable to ensure that substantial chain extension through linking of like blocks does not occur. Thus, for purposes of this invention, one isocyanate moiety of the diisocyanate should preferably be approximately five times more reactive with terminal hydroxyl groups of oxetane and oxirane blocks than the other group. Preferably one isocyanate moiety is at least about ten times more reactive than the other.

Please replace paragraph [0036] with the following.

[0036] In one ~~variant~~ embodiment, the A blocks and B blocks are reacted separately with the diisocyanate, so that there is no competition of the blocks for diisocyanate molecules and each separate end-capping reaction may be carried to substantial completion. The diisocyanate may react more rapidly with one block than the other, but this difference ~~can~~ may be compensated for by a longer reaction time with the slower reacting block. The reactivity of the terminal hydroxyl groups varies according to steric factors and also according to side-chain moieties. Energetic oxetanes, for example, generally have side-chain moieties that are electron-withdrawing, making their terminal hydroxyl groups less reactive. Once end-capped with diisocyanate, the reactivities of the polymers for linking purposes is essentially dependent only upon the reactivity of the free isocyanate, not on the chemical makeup of the polymer chain itself. Thus end-capped (A) blocks are substantially as reactive as end-capped (B) blocks. The end-capping of the oxirane blocks in this manner overcomes the problems associated with linking of oxirane derivative blocks, which have secondary hydroxyl groups.

Please replace paragraph [0037] with the following.

[0037] The end-capping reaction and linking reaction are carried out in a suitable solvent, e.g., one which dissolves the polymer and does not react with the free isocyanate moieties. In a preferred embodiment, the solvent is non-halogenated. Although insubstantial amounts of halogenated solvent may be present, the solution is preferably completely free of any halogenated solvent. The non-halogenated solvent should not react in the urethane reaction (i.e., ~~do~~ should not interfere with the end capping catalyst, such as dibutyl tin dilaurate, or the linking catalyst) and forms an azeotrope with water. The solvent or solvents selected preferably are capable of dissolving more than 25% by weight of the blocks (based on total weight of the solvents and blocks) into solution, more preferably at least 35% by weight into solution, and still more preferably 50% by weight into solution. Representative solvents include cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane; non-cyclic ethers such as ethylene glycol dimethyl ether; ketones such as methyl ethyl ketone (MEK); and esters such as ethyl acetate. Of these, THF is preferred because of its excellent solubility characteristics.

Please replace paragraph [0038] with the following.

[0038] In a ~~preferred one~~ embodiment, the solvent forms an azeotrope with water. In this ~~preferred~~ embodiment, after the blocks are dissolved in excess non-halogenated solvent, the solution may be dried by azeotropic distillation of the solvent, and optionally further concentrated, e.g., via distillation, in the solution to increase the volumetric loading and reaction rate. The blocks then may be end-capped, separately or together, and linked in the same or a different non-halogenated solvent. By distilling off excess solvent to remove water, subsequent reaction with a diisocyanate may proceed without significant interference from competing reactions between the isocyanate moieties and water. Additionally, the solution remains homogeneous and further distillation serves to concentrate the polymer solution, producing higher reaction rates and requiring less reactor capacity. The reaction rates may be improved by conducting the end-capping reaction at elevated temperatures, such as 30° C to 80° C, more preferably 40° C to 60° C. The process may be conducted by a batch or continuous method. For example, the prepolymer and catalyst may be continuously fed through a mixer/extruder into which is injected a diisocyanate and a diol at appropriate feed rates so that urethane linking occurs within the extruder and energetic thermoplastic elastomer is continuously produced for processing.

Please replace paragraph [0061] with the following.

[0061] In a separate 250 ml round bottom flask, 17.94 grams of dry difunctional poly(azidomethyloxirane) with a hydroxyl equivalent weight of 1174 and 6.63 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 2390 were dissolved in 100 ml of tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran via a rotovapor under reduced pressure until 20 grams of solvent remained. To this solution, 0.75 ml of dibutyltin dilaurate and 3.097 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic-driven stirrer. After 1 ~~hours~~ hour, the urethane oligomer was added to this solution, causing it to become steadily more viscous. After 20 minutes, the solution was too viscous to stir with the magnetic-driven stirrer and it was diluted with 20 ml of

dry tetrahydrofuran, and then allowed to react for a further 20 minutes before being poured into methanol in a volume ratio of 1:5. The precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties shown in FIGS. 1 and 2 and set forth below:

$M_n = 26240$

$M_w = 175500$

$M_w/M_n = 6.69$

Please replace paragraph [0062] with the following.

[0062] Molecular weight distribution was determined by gel permeation chromatography using polystyrene standards, with the results shown in FIG. 1. The GPC trace in FIG. 1 demonstrates that the prepolymers were linked to produce a copolymer having a higher molecular weight and dispersivity than the homopolymer blocks. The DMA trace in FIG. 2 shows the melt transition of random block (BAMO-GAP)_n at 75-80° C with a material modulus reducing only slowly before this point.